

DENVER FRONT RANGE STUDY DIOXINS IN SURFACE SOIL

Study 4: Characterization of Dioxins, Furans and PCBs In Soil Samples Collected from Historic Use Areas of the Rocky Mountain Arsenal

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LIST OF ACRONYMS AND ABBREVIATIONS

Ah	aryl hydrocarbon
ATSDR	Agency for Toxic Substances and Disease Registry
CAS	Columbia Analytical Services
COC	Contaminant of Concern
D/F	dioxin/furan
EMPC	Estimated Maximum Potential Concentration
HRGC/MS	High Resolution Gas Chromatography/Mass Spectrometry
LCS	Laboratory Control Sample
MDL	Method Detection Limit
MQL	Method Quantitation Limit
MRI	Midwest Research Institute
NPL	National Priority List
OCF	organochlorine pesticide
PARCC	Precision, Accuracy, Representativeness, Comparability, and Completeness
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzodioxin
PCDF	polychlorinated dibenzofuran
PE	Performance Evaluation
ppt	parts per trillion (1 microgram per kilogram)
QA/QC	Quality Assurance/Quality Control
QATS	Quality Assurance Technical Support
RMA	Rocky Mountain Arsenal
RPD	Relative Percent Difference
SOP	Standard Operating Procedure
TCDD	2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin
TEF	Toxicity Equivalency Factor
TEQ	2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin equivalents
TOC	Total Organic Carbon
TSY	Toxic Storage Yard
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

LIST OF CHEMICAL ABBREVIATIONS

HpCB	heptachlorobiphenyl
HpCDD	heptachlorodibenzodioxin
HpCDF	heptachlorodibenzofuran
HxCB	hexachlorobiphenyl
HxCDD	hexachlorodibenzodioxin
HxCDF	hexachlorodibenzofuran
OCDD	octachlorodibenzodioxin
OCDF	octachlorodibenzofuran
PeCB	pentachlorobiphenyl
PeCDD	pentachlorodibenzodioxin
PeCDF	pentachlorodibenzofuran
TCB	tetrachlorobiphenyl
TCDD	2,3,7,8-tetrachlorodibenzo- <i>p</i> -dioxin
TCDF	tetrachlorodibenzofuran

1.0 INTRODUCTION

1.1 Site Description

The Rocky Mountain Arsenal (RMA) is a parcel of approximately 27 square miles of land located north-east of Denver, Colorado. The RMA was previously used by the US Army for manufacturing and testing of munitions, and was subsequently used by Shell Oil Company for the manufacture of pesticides. Because of extensive chemical contamination in the central portion of the site, the United States Environmental Protection Agency (USEPA) became involved in studies to clean up RMA in 1982, and the site was placed on National Priorities List (NPL) in 1987. The chemicals of principal health concern at RMA vary from location to location, and include pesticides, metals, solvents, chemical process intermediates, and chemical warfare agents. In particular, several organochlorine pesticides (OCPs), mainly aldrin and dieldrin, are major contaminants of concern (COCs), as well as a number of their intermediates and degradation products (USEPA 1999).

Some members of the public stated they were concerned that RMA might be contaminated with dioxins. A review of this question was performed by Gannett Fleming (1999), and USEPA Region 8 concluded that data available at the time were insufficient to determine whether dioxins should or should not be considered chemicals of potential concern at RMA. In order to investigate this question, USEPA Region 8, working in cooperation with the State of Colorado and the Rocky Mountain Arsenal Remedial Venture Office, has undertaken a series of studies to characterize the levels of dioxins in on-site and off-site soils. This report summarizes the results of a study designed to characterize dioxin levels in the South Plants area of RMA (this was the core area historically used for pesticide manufacture), as well as at a number of other on-site locations where past land uses might have led to increased levels of dioxins.

Other reports which are part of this project and which provide additional information on the absolute and relative level of dioxins in on-site and off-site soils include:

Denver Front Range Study. Dioxins in Surface Soil. Study 3: Western Tier Parcel, Rocky Mountain Arsenal (USEPA 2001a)

Denver Front Range Study. Dioxins in Surface Soil. Study 2: Characterization of Dioxins, Furans and PCBs in Random Soil Samples Collected from the Rocky Mountain Arsenal (USEPA 2001b)

Denver Front Range Study. Dioxins in Surface Soil. Study 1: Characterization of Dioxins, Furans and PCBs In Soil Samples Collected from the Denver Front Range Area (USEPA 2001c)

1.2 Definition of Dioxins

"Dioxin" is usually used as a synonym for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). The toxicity of TCDD is believed to be initiated by binding of the TCDD molecule to a cellular protein referred to as the aryl-hydrocarbon (Ah) receptor. However, there are many different chemicals besides TCDD that can bind to this receptor and trigger some or all of the toxic responses that are associated with TCDD exposure. This includes some other members (congeners) of the polychlorinated dibenzodioxin (PCDD) class, as well as some polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), other types of halogenated (e.g., brominated) dioxins and furans, as well as various other chlorinated hydrocarbons (e.g. chlorinated naphthalenes). For the purposes of this report, the term "dioxins" is meant to refer to the set of 29 congeners in the polychlorinated dioxin/furan/biphenyl group that bind to the aryl hydrocarbon (Ah) receptor and possess toxic characteristics similar to those of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). These 29 congeners are listed in Table 1.

In this study and report, greatest emphasis is placed on the 17 PCDD and PCDF congeners with TCDD-like activity, since PCBs are not considered to be chemicals of concern at RMA, and because the current USEPA soil screening levels for dioxins (USEPA 1998) are based only upon these congeners. However, the 12 PCB congeners with TCDD-like activity were included in the study and analyses for reasons of a) completeness for background characterization, and b) to help resolve mass-balance comparisons with TCDD bioassays that were conducted for RMA tissue samples and which could be performed (if needed) on soil samples.

Relative Toxicity of Dioxin Congeners

Dioxins are of potential health concern because they may pose an increased risk of cancer and other non-cancer adverse health effects at extremely low levels of exposure. However, not all dioxin congeners are equally toxic. The relative toxicologic potency of a congener, compared to that of the most toxic form (2,3,7,8-TCDD), is expressed in terms of the Toxicity Equivalency Factor (TEF). Table 1 lists the current consensus TEF values for mammals (including humans), birds, and fish. These TEF values were developed by a panel of experts assembled by the World Health Organization (WHO) (Van den Berg et al. 1998), and have been adopted for use by the USEPA (USEPA 2000). It should be noted that TEFs are often based on limited data, and so

Table 1. List of Analytes and TEFs

Class	Target Analyte	TEF		
		Mammals	Birds	Fish
Dibenzo-p-dioxins (PCDDs)	2,3,7,8-TCDD	1	1	1
	1,2,3,7,8-PeCDD	1	1	1
	1,2,3,4,7,8-HxCDD	0.1	0.05	0.5
	1,2,3,6,7,8-HxCDD	0.1	0.01	0.01
	1,2,3,7,8,9-HxCDD	0.1	0.1	0.01
	1,2,3,4,6,7,8-HpCDD	0.01	< 0.001	0.001
	OCDD	0.0001	0.0001	<0.0001
Dibenzofurans (PCDFs)	2,3,7,8-TCDF	0.1	1	0.05
	1,2,3,7,8-PeCDF	0.05	0.1	0.05
	2,3,4,7,8-PeCDF	0.5	1	0.5
	1,2,3,4,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,7,8,9-HxCDF	0.1	0.1	0.1
	2,3,4,6,7,8-HxCDF	0.1	0.1	0.1
	1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01
	1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01
	OCDF	0.0001	0.0001	<0.0001
PCBs	3,3',4,4'-TCB (77)	0.0001	0.1	0.0005
	3,4,4',5-TCB (81)	0.0001	0.05	0.0001
	3,3',4,4'-5-PeCB (126)	0.1	0.1	0.005
	3,3',4,4',5,5'-HxCB (169)	0.01	0.001	0.00005
	2,3,3',4,4'-PeCB (105)	0.0001	0.0001	< 0.000005
	2,3,4,4',5-PeCB (114)	0.0005	0.0001	< 0.000005
	2,3',4,4',5-PeCB (118)	0.0001	0.00001	< 0.000005
	2',3,4,4',5-PeCB (123)	0.0001	0.00001	< 0.000005
	2,3,3',4,4',5-HxCB (156)	0.0005	0.0001	< 0.000005
	2,3,3',4,4',5'-HxCB (157)	0.0005	0.0001	< 0.000005
	2,3',4,4',5,5'-HxCB (167)	0.00001	0.00001	< 0.000005
	2,3,3',4,4',5,5'-HpCB (189)	0.0001	0.00001	< 0.000005

TEF = Toxicity Equivalency Factor

TEF values are consensus estimates recommended by WHO (Van den Berg et al. 1998)

they are recommended for use as only approximations of the relative toxicity of each congener, rounded to the nearest half order of magnitude.

Calculation of TCDD-Equivalents (TEQ) in Soil

The aggregate toxicity of a mixture of different dioxins in an exposure medium (soil, food web items, water, etc.) is a complex function of the following variables:

- a) the concentration of each congener in the medium
- b) the chronic average daily intake of the medium
- c) the absorption of each congener from that medium
- d) the toxicokinetics (distribution, metabolism, and elimination) of the congeners
- e) the relative biological potency of the congeners

Thus, calculation of health risk from exposure to soil that contains a mixture of congeners must take all of these variables into account. However, for purposes of screening-level evaluations of dioxin concentrations in soil samples, it is usually most convenient to calculate the concentration of TCDD-Equivalents (TEQ) present in the soil as the TEF-weighted sum of each of the 29 dioxin-like congeners (17 dioxins and furans, plus 12 PCBs), as follows:

$$\text{TEQ}(\text{total}) = \sum_{i=1}^{29} (C_i \cdot \text{TEF}_i)$$

In cases where interest is focused on the contribution of PCDDs and PCDFs only (i.e., PCBs not included), the value is calculated as:

$$\text{TEQ}(\text{D} / \text{F}) = \sum_{i=1}^{17} (C_i \cdot \text{TEF}_i)$$

It is important to understand that this application of TEFs to the calculation of soil TEQ values is appropriate only for screening level purposes. This is because TEFs are derived from, and thus should only be applied to, biological endpoints (e.g., embryotoxicity). The soil TEQ approach does not account for the potential influences of differential absorption, metabolism, distribution, and excretion of different congeners from soil, and risk assessors should account for these uncertainties in the interpretation of the soil TEQ values.

1.3 Human Health Based Reference Values for Dioxins in Soil

The USEPA has currently established a default concentration value of 1,000 parts per trillion (ppt) TEQ in surface soil as a concentration that is not of cancer or non-cancer concern for lifetime exposure of residents (USEPA 1998a), even when no other site-specific data are

known. For commercial and industrial land uses, USEPA guidelines identify 5,000 to 20,000 ppt TEQ as the concentration of concern in soil. These soil screening concentrations are based only upon the 17 TCDD-like PCDDs and PCDFs, calculated using the TEFs for mammals recently recommended by the WHO (Van den Berg et al. 1998).

The Agency for Toxic Substances and Disease Registry (ATSDR) has also established an interim policy guideline for human (residential) exposure to dioxin and dioxin-like compounds in soil (De Rosa et al. 1997). ATSDR identifies a concentration of 50 ppt TEQ in soil as a "screening level," below which no further investigation or characterization will usually be required. ATSDR identifies a concentration of 1,000 ppt TEQ as an "action level," indicating that public health actions such as surveillance, research, health studies, community education, or exposure investigations should be considered. Concentrations between 50 ppt and 1000 ppt TEQ are identified as "evaluation levels," indicating that further investigation of site-specific factors regarding the extent and possible public health implications of the exposure may be warranted.

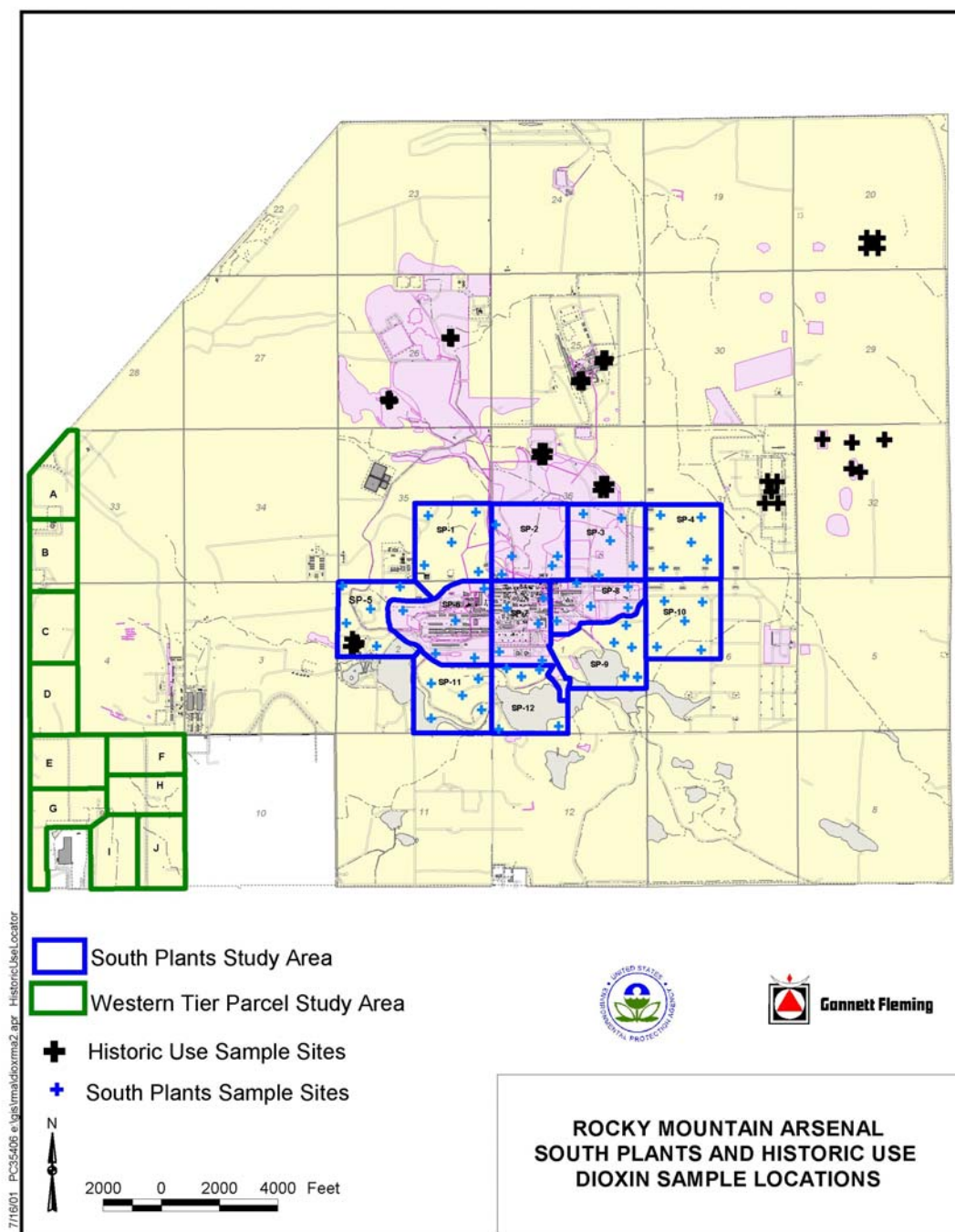
The USEPA is in the process of completing a comprehensive reassessment of dioxin toxicity, and has tentatively concluded that the carcinogenic and non-carcinogenic potency of dioxins may be somewhat greater than previously believed (USEPA 2000). However, until a complete peer review and cross-program policy assessment of the impacts of this report can be performed, USEPA recommends that the 1,000 ppt TEQ concentration in surface soil continue to be used as a soil screening level for residential land uses (USEPA 1998a), and that 5,000 ppt TEQ be used as a frame of reference for assessing exposure of commercial workers.

2.0 METHODS

A detailed description of the rationale, methods, and Standard Operating Procedures (SOPs) used in this study is provided in the Project Plan for the study (USEPA 1999). A summary of key elements of the study design and of the methods employed is presented below.

2.1 Sampling Locations

Figure 1 provides a map of RMA, and indicates the locations of samples collected for this study. Details of the sampling locations are provided in Appendix C.

Figure 1. South Plants and Historic Use Sampling Locations

The area of chief potential concern is the South Plants area, located in the south-center of the site. In the past, this area was the chief location of pesticide and chemical manufacturing activities. In order to plan the collection of samples in this area, a 12-section grid was laid out over the South Plants area as shown by the blue lines in Figure 1. Within each grid, a set of five grab samples were collected from random sampling locations, as shown by the blue crosses. These five grab samples were combined into a single composite sample (one for each grid), as described below.

In addition to South Plants, there are a number of other areas at RMA where historic land uses or waste disposal activities might have resulted in increased levels of dioxins in soil. These areas of potential concern are described in Table 2. One composite sample (prepared from five randomly located grab samples, as described above) were collected from each of these 10 “purposeful” sampling locations, as shown by the black crosses in Figure 1.

2.2 Sample Collection and Storage

Because dioxins nearly always bind tightly to soil, it is expected that any dioxin contamination in soil attributable to atmospheric fallout, application of pesticides, or surface disposal of dioxin-contaminated material will be restricted mainly to the surface. Thus, surface soil is the exposure medium of chief concern for both human and ecological receptors. Therefore, all soil samples collected for this study were grab samples collected at 0-2 inches in depth.

Samples were collected using clean techniques that included use of disposable stainless steel trowels (one per sampling location) and plastic gloves. A ruler was used to ensure that the actual depth to which soil was collected was within $\frac{1}{2}$ inch of the target (i.e., a bottom depth of no less than 1.5 inches and no greater than 2.5 inches). Loose debris and most gravel or pebbles were removed from the soil sampling site. The surface soil was placed directly into a clean 16-ounce amber glass jar, filled to capacity (about 500 grams of soil), sealed with a teflon-lined lid, and stored in these bottles at room temperature in the dark until shipped in sealed plastic coolers with frozen ice-packs and water temperature tubes that helped ensure no excess heating occurred during transportation to the processing laboratory.

2.3 Sample Preparation

All soil samples collected in the field were submitted under chain-of-custody to Columbia Analytical Services (CAS) for sample preparation. Each sub-sample from a sub-parcel was air-dried and weighed, followed by coarse-sieving through a #10 (2 millimeter) stainless steel screen

Table 2. RMA Purposeful Sample Locations and Descriptions

Sample #	Location/Description
P1	Sample P1 is located just east of the southeast corner of former Basin F in the Basin F Exterior Soils. This sample will evaluate soils that have been impacted by the windblown distribution of Basin F liquids from the spray evaporation system.
P2	Sample P2 is located in the south central portion of Section 20 in the ash disposal area. This sample will evaluate soils/ash where incinerator and electrostatic precipitator ash from Mustard demilitarization operations were disposed.
P3	Sample P3 is located in secondary Basin D in Section 26. This sample will evaluate soils impacted by the disposal of liquid wastes from RMA production areas.
P4	Sample P4 is located just east of the North Plants production facility. This sample will evaluate soils potentially impacted by the incineration operations in North Plants.
P5	Sample P5 is located within the North Plants production facility. This sample will evaluate soils potentially impacted by GB operations within North Plants as well as the incineration operations in North Plants.
P6	Sample P6 is located in the Toxic Storage Yard (TSY) in Section 31. This sample will evaluate soils potentially impacted by spills of various materials stored in the TSY.
P7	Sample P7 is located in former burn pits and burial trenches located in Section 32. This sample will evaluate soils impacted by the pits and trenches.
P8	Sample P8 is located just southwest of the trash incinerator in Section 36. This sample will evaluate soils potentially impacted by emissions from the trash incinerator.
P9	Sample P9 is located east of the Complex/Army Trenches in Section 36. This sample will evaluate soils potentially impacted by windblown dispersion of waste and emissions from disposal and burning conducted in the trenches.
P10	Sample P10 is located near the USFWS Visitor Center in Section 2. This sample will evaluate soils in areas which are frequently visited by the public.

(Provided by CDPHE, M. Kadnuck, 12/99)

The fraction passing the coarse screen was referred to as the “bulk” fraction. About 100 grams of mixed bulk soil from each of the five sub-samples for a sub-parcel was then combined to produce a composite sample of about 500 grams to represent the sub-parcel surface soil. After mixing the composite bulk soil, approximately 26 grams of the bulk composite sample was placed in a clean amber glass jar and stored for possible future use. The remainder of the composited bulk sample was further sieved through a 60-mesh (250 micrometer) stainless steel screen in order to isolate soil particles less than 250 micrometers in diameter. This is referred to as the “fine” fraction. The fine-sieved soil samples were thoroughly mixed, and placed into four new amber sample bottles, with each bottle containing about 26 grams of the fine-sieved composited soil. These four aliquots of fine-sieved soil were intended to be as identical as possible, for use in reanalysis (if needed) and for establishing intra-laboratory and inter-laboratory reproducibility (precision) for quality control purposes. The remainder of each sub-sample soil fraction was retained and stored under chain of custody by USEPA Region 8, in case there was a need to analyze any of the individual sub-samples separately. All processed soil samples were sent under chain of custody to the USEPA Regional Laboratory in Golden, CO, for storage and for organization of samples for later shipments to the analytical laboratory in Kansas City, MO.

The “fine” fraction was isolated for chemical analysis because it is believed that fine soil particles can electrostatically adhere to skin and thus are more likely be ingested by hand to mouth contact than coarse particles. Hence it is concluded that the fine soil fraction is the most relevant media for use in evaluating human health risk. The bulk soil samples were retained for purposes of evaluating the potential enrichment of TEQ concentrations in the fine-sieved fraction due to small soil particles having greater surface to mass ratios than their bulk soil counterparts. It should be noted that most historic soil sampling studies for dioxins have only evaluated bulk soils, and so consideration needs to be given when comparing historic bulk dioxin results and the results for dioxin TEQs in this study’s fine soil samples. If enrichment is present, it would cause the fine soil fractions to have greater concentrations of TEQs than their corresponding bulk counterparts, and bulk soil results would tend to underestimate exposure.

2.4 Sample Analysis

Following sample preparation as described above, samples were submitted by USEPA Region 8 under chain of custody to Midwest Research Institute (MRI) for congener-specific analysis of PCDDs, PCDFs, and PCBs. This type of analysis requires sophisticated extraction and clean-up procedures to accurately measure all of the various forms of PCDDs, PCDFs, and PCBs, as detailed in Standard Operating Procedure 11 of the Project Plan USEPA (1999). In brief, the congeners are determined using an isotope dilution method via high resolution gas chromatography/mass spectrometry (HRGC/HRMS). Samples are fortified with known quantities of ¹³C-labeled PCDD/PCDF/PCB isomers and extracted with organic solvents, using

two columns so that all 12 PCBs can be retained for analysis. Before cleanup of the extracts, the analytes are exchanged into hexane and fortified with ^{37}Cl -labeled 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. Finally, the extracts are sequentially partitioned against concentrated acid and base solutions.

The Method Detection Limit (MDL) for this study-specific analytical method was defined as an analyte signal that was 2.5 times the average background signal ("noise"). An estimate of the average signal noise is available for each analyte in each sample, so the MDL varies from sample to sample and from analyte to analyte. The Method Quantitation Limit (MQL) is based partly on the lowest calibration standard used, and was defined as a signal that was 10-times the average signal noise. Because the noise level varied from sample to sample and analyte to analyte, MDLs and MQLs also varied from sample to sample and from congener to congener. Most PCDD/PCDF congeners had MQL values between 0.4 and 7.2 ppt, and most PCB congeners had MQLs between 1.4 and 71 ppt.

2.5 Quality Assurance

A number of steps were taken to obtain data that would allow an assessment of the quality and reliability of the data collected, so that assessments of the scientific usability of the data could be made and defended. The analytical laboratory routinely processed and analyzed "lots" (batches) of 20 samples at a time. Of these 20 samples, two were used for laboratory control samples (LCS) and blanks. Therefore, 18 samples were usually available for USEPA to submit to MRI as a batch. In general, these 18 samples were comprised of 14 field samples plus four Quality Control (QC) samples, as described below.

Performance Evaluation Samples

Performance Evaluation (PE) samples are samples of soil that contain known quantities of analyte and that are submitted blind to the analytical laboratory. In this study, three different PE samples were used. These were obtained from USEPA's Quality Assurance Technical Support (QATS) laboratory. Nominal values (ppt as TEQ in bulk soil, based on the 17 PCDD/PCDF congeners only) are listed below:

Table 3. Nominal TEQ(D/F) Concentrations in PE Samples

PE Sample (Bulk Soil)	Nominal TEQ(D/F) (ppt)
Native western soil (estimated value)	< 2
Low standard (certified value)	35
Medium standard (certified value)	59

One aliquot of each these three PE samples from QATS was submitted to the laboratory along with each batch of field samples.

Field Splits and Duplicates

A field duplicate is a second sample of soil collected simultaneously with the first sample. In this case, field duplicates were collected by alternating scoops of soil into two bottles with separate and random sample identification numbers. A field split is a sample that is generated by dividing a single field sample into two parts. As described above, in this study every field sample was dried and sieved by CAS, and this fine material was divided into four essentially identical aliquots of 26 grams each. EPA Region 8 selected random samples to submit as split samples, and a second bottle of these samples was assigned a new random sample identification number and submitted in random order for analysis by MRI. Analysis of these types of samples provided data on the variability within and between related samples. One sample of this type (either field split or field duplicate) was submitted to the laboratory (blind) with each set of 14 field samples.

Laboratory Quality Control Samples

Internal laboratory quality control samples are samples prepared and run by the laboratory in a non-blind fashion to monitor the performance of the analytical method. Laboratory QC samples included Method Blanks (analyte-free soil), Laboratory Control Samples (similar to PE samples, but the identity and true concentration are known to the laboratory), and optionally Method Duplicates (investigative samples that are split prior to sample preparation at the analytical laboratory). As noted above, two samples in each batch were used by the laboratory for laboratory QC samples.

2.6 Data Validation/Verification

Validation of analytical results was conducted according to SOP 803 (revision 1) of the Project Plan (USEPA 1999). This validation method was tailored to match the site-specific method used to analyze the 29 dioxin-like congeners in soils. An independent contract chemist team, with expertise in validation of PCDD, PCDF, and PCB analytical results, conducted the analytical reviews. Full validation was performed for all samples.

Major analytical factors and QA/QC performance were reviewed against defined Precision, Accuracy, Representativeness, Comparability, and Completeness (PARCC) criteria to ensure that results were reliable and usable for the objective identified in the Project Plan. Narratives were produced for each analytical lot to describe the results of the data validation for that lot. Each data value (i.e., each concentration value) was assigned a data usability flag, if needed, using the data quality flag codes presented in Table 4. In accordance with USEPA data usability guidelines (USEPA 1992), these flags were used for producing two alternative data sets:

- 1) a semi-quantitative set of results in which congeners that yielded signals below the sample-specific detection limit for that congener (signal/noise ratio less than 2.5) were evaluated by assuming a concentration value equal to $\frac{1}{2}$ the detection limit for that congener, and other flagged data were adjusted according to the rules shown in Table 4. This is referred to in this report as the “**Full**” data set.
- 2) a quantitative set of results based only on those congeners that have no disqualifying flags (D, NJ, R and LT), or have adjusted quantitative values as described in Table 4. This is referred to in this report as the “**Quant**” data set.

These two datasets were prepared to help evaluate the magnitude of effects of estimated values from the Full dataset on TEQs, and to show how the quantitative subset of results can be properly derived to statistically evaluate the profiles of congeners in soils. In general, the Full TEQ(D/F) results are considered to be the most relevant in evaluating potential health risks from dioxins.

3.0 RESULTS

Detailed analytical results for each field sample are presented in Appendix A1, and detailed results for each QA sample run as part of this study are presented in Appendix A2. Graphical representations are presented in Appendix B. The results are summarized below.

Table 4. Definition, Application, and Uses of Data Flags

Validation Flags	Meaning of Flags for Dioxin Analyses in Soils and Tissues by the MRI Lab	Data Usability (a)	
		Full data set used (<i>semi-quantitative</i>)	Quantitative (qualified sub-set used)
E	<u>Estimated Maximum Potential Concentration</u> ; the relative ion abundance ratios did not meet the acceptance limits.	use value	use ½ value
D	EMPC is caused by <u>polychlorinated Diphenyl ether</u> interference.	use ½ value	don't use
B	Analyte was detected in associated <u>Method Blank</u> , sample concentration <5x MB concentration.	use value	use ½ value
C	Concentration is <u>above upper Calibration Standard</u> ; result is an estimate, flagged C by lab and J added by validator.	use value	use value
I	<u>Recovery of 13C-labeled Isotopic analyte</u> outside of criteria	use value	use value
J	<u>Estimated</u> ; e.g., isotopic standard is outside CCAL range, native analyte recovery in LCS is outside criteria, etc.	use value	use ½ value
NJ	<u>Presumptive evidence</u> for the presence of an analyte with an estimated value; if used for 2378-TCDF, see "U" below.	use ½ value	don't use
S	Peak is <u>Saturated</u> ; result, if calculated, is flagged by the validator as an estimate - "J".	use value	use value
U	<u>Unconfirmed</u> : column is not specific for 2,3,7,8-TCDF; confirmation not requested. Validator now uses "NJ" flag.	use value	use ½ value
R	<u>Rejected</u> : result is invalid and <u>not usable</u> .	use ½ MDL	don't use
<i>use of MRI Laboratory's reported "LT" (less than) values <MQL (10 x Signal:Noise)</i>			
LT <i>applied first to data, then apply flags!</i>	"LT" is not a true "flag", but if a LT result is a " detect " above the MDL (2.5 x Signal:Noise = lab EDL), then	use value	use ½ value
	"LT" is not a true "flag", but if a LT result is a " non-detect " below the MDL (2.5 x Signal:Noise = lab EDL), then	use ½ EDL	don't use

(a) In accord with concepts in the 1992 EPA Data Usability for Risk Assessment in Superfund guidance (USEPA 1992), data quality flags are used to produce two data-sets: 1) a "**Full**" set of semi-quantitative results with an **actual** or a **proxy** value for each of the measured congeners; and 2) a more "Quantitative" but limited set of results that has more certain identification and more accurate quantities of congeners which have **no disqualifying flags** (**D**, **NJ**, **R** or **LT**), but can use **limited proxies** (**E**, **B**, **J** or **U**). This distinction is made to better understand and limit artifactual impacts of the *less certain estimated values* on TEQs, analyzing the degree of this sensitivity to trace-level "noise" by comparing TEQs from these two data sets. In addition, congener profile pattern analysis should only use the analytes that are quantifiable (above the MQL).

3.1 Data Validation Results

Full validation of the data found the analytical results to be usable, as qualified with the appropriate data quality flags (see Appendix A).

3.2 TEQ Values in Field Samples

Table 5 presents the results (expressed as ppt of TEQ) for each of the 12 composites samples collected from the South Plants area and for each of the 10 purposeful samples collected from the historic use areas at RMA.

For the samples collected from the South Plants area, Full TEQ(D/F) values ranged from about 2 to 94 ppt, while Quant TEQ(D/F) values ranged from about 1 to 84 ppt. The spatial pattern of the Full TEQ(D/F) values for samples from South Plants is shown in Figure 2. As seen, the highest values (20-94 ppt) occur in the center of the South Plants area, with concentrations of 2-6 ppt in the perimeter grids. This spatial pattern is consistent with the hypothesis that low levels of dioxins were formed and released to soil during historic operations at the South Plants area, but that the contamination is largely restricted to the manufacturing area, and rapidly decreases as a function of distance from the historic source.

For the 10 purposeful samples collected from the different historic use areas of RMA, Full TEQ(D/F) values ranged from 1.2 to 13.5 ppt, while Full TEQ(Total) values ranged from 1.4 to 48.8 ppt. The spatial pattern of the Full TEQ(D/F) values for the purposeful samples from the historic use areas of RMA is shown in Figure 3. As seen, the highest values (10-14 ppt) occur at Stations P-3, P-4, P-5 and P-6, which are associated with the following:

Sample P-3 is located in secondary Basin D in Section 26. This sample is composed of soils impacted by the disposal of liquid wastes from RMA production areas.

Sample P-4 is located just east of the North Plants production facility. This sample is composed of soils potentially impacted by the incineration operations in North Plants.

Sample P-5 is located within the North Plants production facility. This sample is composed of soils potentially impacted by GB operations within North Plants as well as the incineration operations in North Plants.

Sample P-6 is located in the Toxic Storage Yard (TSY) in Section 31. This sample is composed of soils potentially impacted by spills of various materials stored in the TSY

Figure 2. Full TEQ(D/F) Levels in Soil at the South Plants Area of RMA

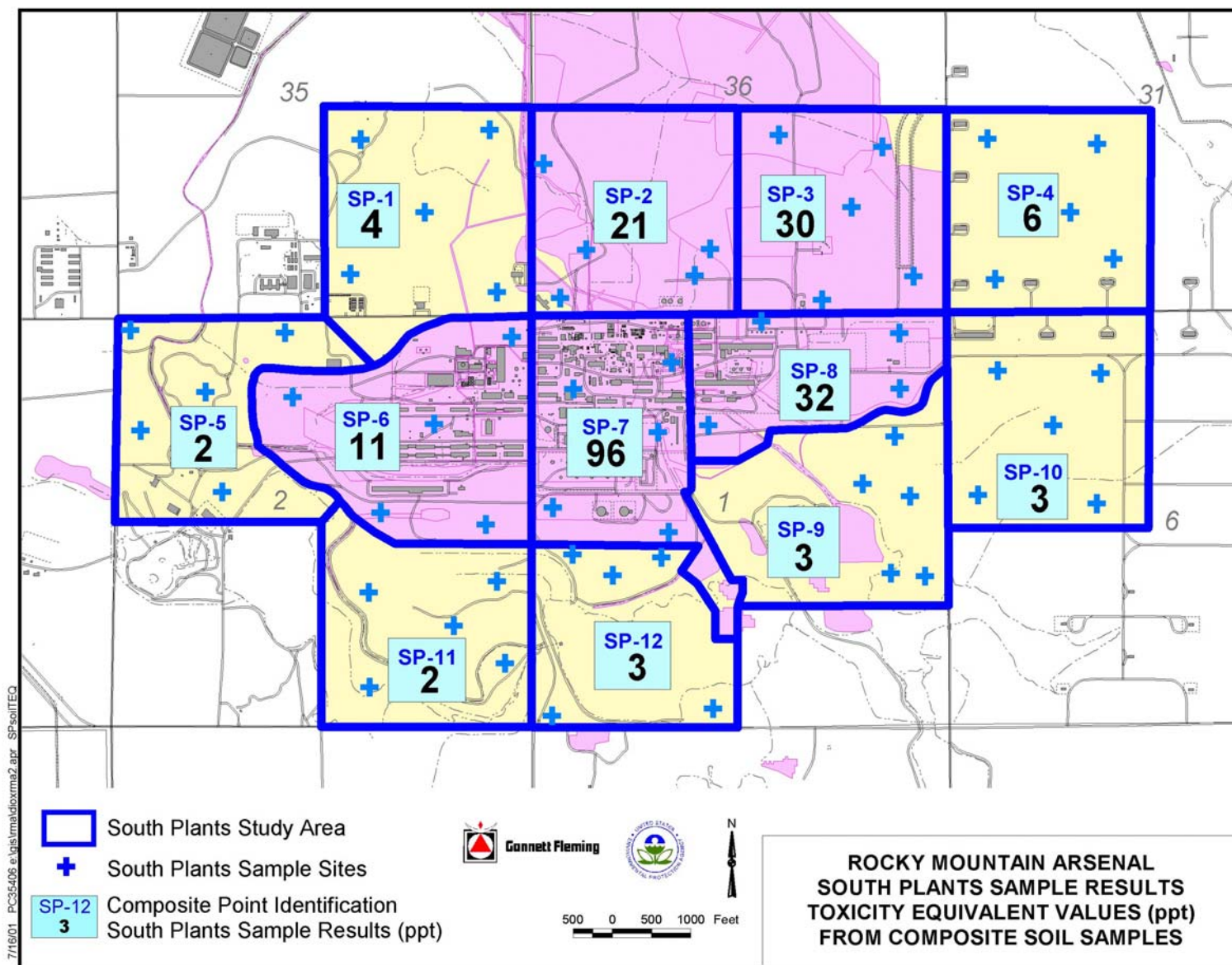
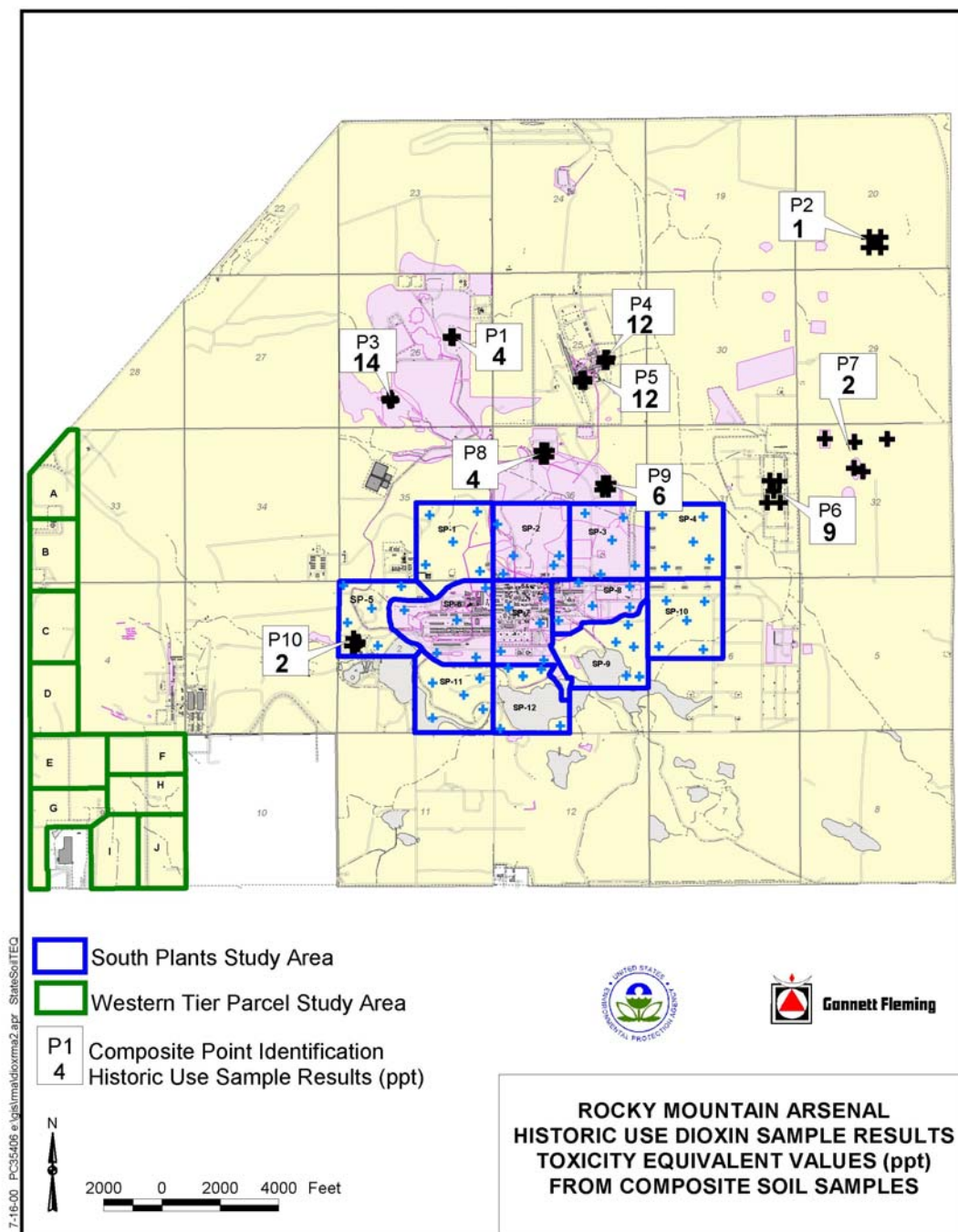


Figure 3. Full TEQ(D/F) Levels at Historic Use Areas of RMA



Full TEQ(D/F) concentrations at the other sampling stations range from 1-5 ppt. These results are consistent with the hypothesis that dioxins were released to some soil locations during historic operations at RMA, but that the magnitude of the contamination is low.

3.3 Comparison to Risk-Based Guidelines

In accordance with the Project Plan developed before implementation of this study, the potential health risk to on-site workers from future exposures to dioxins in soil was evaluated by comparing the TEQ concentration value in each composite sample with the USEPA default health-based reference range of 5,000-20,000 ppt identified by USEPA as the potential level of concern for workers (EBASCO 1994). Inspection of Table 5 reveals that all of the samples collected in this study, including the most heavily impacted samples from the South Plants area and other historic use areas, are all far below the level of potential health concern to workers. This is shown graphically in Figure 4.

One potential limitation of this conclusion is that the soil samples being compared to the EPA are all composites; that is, the concentration value for a composite might be determined by one high sub-sample value mixed with four lower values. However, this is not of significant concern, since it is the mean value, not individual sub-sample values, within an exposure unit that is the determinant of human health risk to a worker moving at random within the exposure area. Further, the highest possible concentration that could occur in any one sub-sample of a 5-point composite is five-times the composite value (assuming that all four of the other sub-samples had a concentration of zero), and even in this worst case scenario, the highest Full TEQ(D/F) that could have occurred in any sub-sample (that for sample SP-7) is 468 ppt TEQ(D/F), which is still more than 10-times below the health effect level of concern of 5,000 ppt established by EPA for workers at RMA.

3.4 Contribution of PCBs

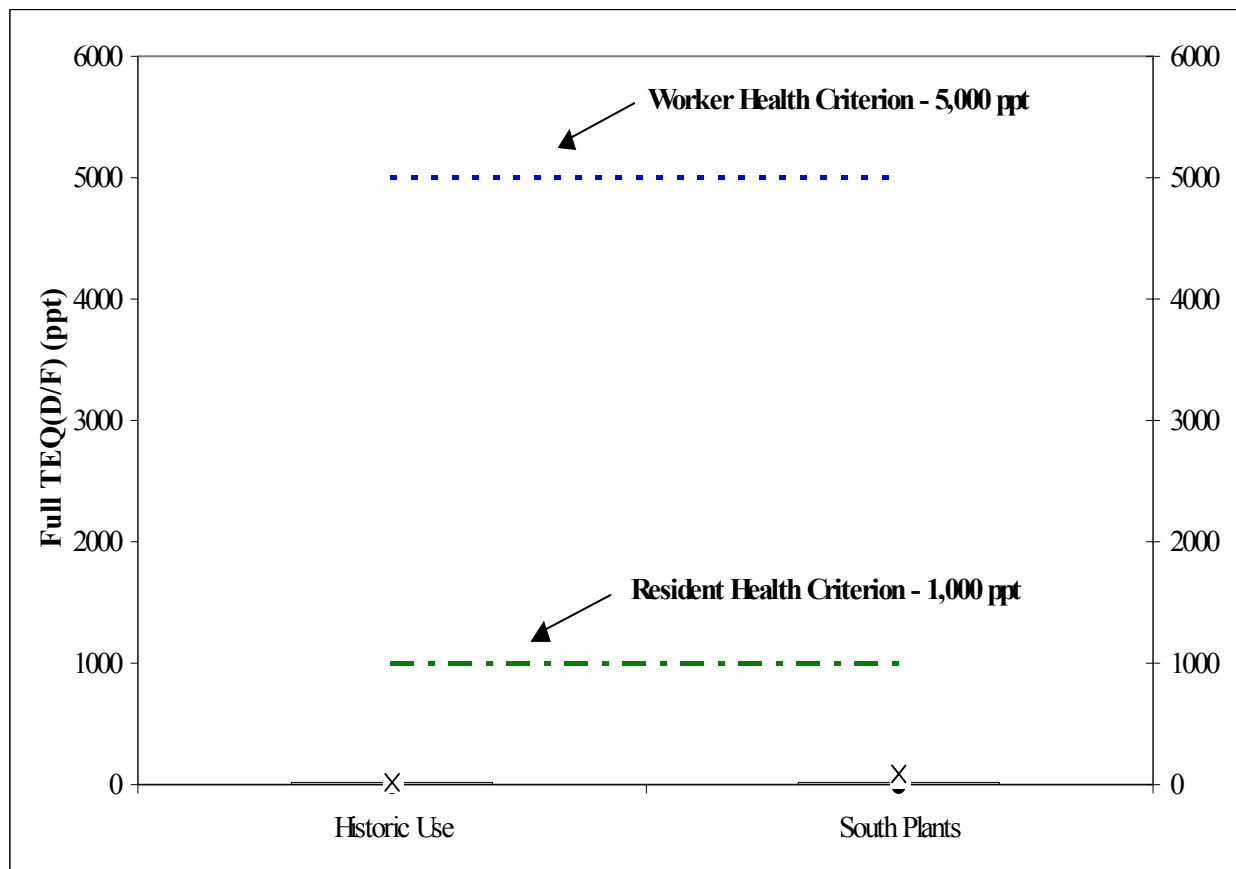
As shown in Table 5, for the 12 samples from the South Plants area, PCBs contribute an average of about 17% to the Full TEQ(Total) value. For the 10 purposeful samples from the historic use areas, the contribution of PCBs is somewhat higher (about 33% on average). This is due mainly to sample P-5 which contains a substantially higher level of PCBs (about 37 ppt Full TEQ) than most other samples, which are all less than 5 ppt Full TEQ(PCBs).

3.5 Contribution of Congeners Below the Quantitation Limit

As noted above, in the calculation of the Full TEQ value for a sample, all congeners that were below the detection limit (signal/noise ratio < 2.5) were evaluated by assuming a

Table 5. Soil TEQ Values for Historic Use Areas at RMA

Location	Sample	TEQ(D/F) (ppt)		TEQ(PCBs) (ppt)		TEQ(Total) (ppt)	
		Full	Quant	Full	Quant	Full	Quant
South Plants	SP-1	4.4	2.7	1.2	1.1	5.6	3.7
	SP-2	20.4	17.3	1.7	1.6	22.1	18.9
	SP-3	29.3	26.4	3.6	3.2	32.9	29.7
	SP-4	5.5	4.3	0.6	0.5	6.0	4.9
	SP-5	1.8	1.1	0.9	0.8	2.7	1.9
	SP-6	10.5	9.2	3.6	3.1	14.1	12.3
	SP-7	93.6	83.8	7.3	6.5	100.9	90.2
	SP-8	31.2	26.9	2.7	2.5	33.9	29.4
	SP-9	3.3	2.6	0.6	0.3	3.9	2.9
	SP-10	2.9	2.2	0.4	0.4	3.3	2.6
	SP-11	2.1	1.4	0.9	0.8	3.0	2.2
	SP-12	3.0	2.3	0.6	0.6	3.7	2.8
Purposeful	P-1	3.6	2.1	1.7	1.6	5.4	3.7
	P-2	1.2	0.7	0.3	0.2	1.4	0.9
	P-3	13.5	12.3	3.2	3.1	16.8	15.3
	P-4	12.5	12.0	2.9	2.8	15.4	14.8
	P-5	11.4	10.6	37.4	18.8	48.8	29.5
	P-6	9.6	9.4	0.9	0.8	10.5	10.3
	P-7	1.6	1.2	0.3	0.3	1.9	1.5
	P-8	3.6	3.3	2.3	2.2	5.9	5.5
	P-9	5.5	4.7	1.8	1.7	7.3	6.4
	P-10	2.0	1.5	4.7	4.2	6.7	5.7

Figure 4. Comparison of TEQ Values to EPA's Health-Based Criterion

concentration value equal to $\frac{1}{2}$ the detection limit. This is the approach that is normally used to evaluate chemicals of concern at Superfund sites (USEPA 1989). In order to evaluate the relative contribution of congeners that were either not detected, or else were present at such low concentrations that their true concentration could only be estimated, a second calculation of "Quant" TEQ was performed, which included only those congeners that were detected above the quantitation limit (signal/noise > 10). Other occasional adjustments to reported concentrations of congeners were made when certain qualifier flags were assigned to the result, based on the criteria shown in Table 4.

For samples from the South Plants area, the average ratio of Full TEQ(D/F) to Quant TEQ(D/F) was about 1.31. For the purposeful samples, the average ratio of Full TEQ(D/F) to Quant TEQ(D/F) was about 1.26. This indicates that congeners that are present below the quantitation limit contribute an average of about 26%-31% to the estimated TEQ(D/F) at these historic use areas of RMA.

3.6 Comparison of Bulk to Fine Samples

As noted earlier, all samples were prepared by sieving to isolate the "fine" fraction of particles less than 250 micrometers in diameter, since it is believed that this size fraction is likely to be of greater relevance to human exposure than the bulk fraction. However, since most other studies of dioxin concentrations in soil have used un-sieved soil, four samples of bulk soil were also analyzed to allow a comparison of concentration values in the bulk and fine fractions. The results are summarized below.

Table 6. Comparison of Bulk and Fine Soil Samples

Sample	Full TEQ(D/F) (ppt)			Full TEQ(total) (ppt)		
	Bulk	Fine	Ratio(a)	Bulk	Fine	Ratio(a)
SP-2	18.1	20.4	1.1	19.8	22.1	1.1
SP-3	25.2	29.3	1.2	28.5	32.9	1.2
SP-6	10.0	10.5	1.1	13.2	14.1	1.1
SP-7	74.6	93.6	1.3	80.9	100.9	1.2

Ratio = Fine/Bulk

As seen above, even though data are available for only four samples, the results suggest that there is an enrichment of about 10-20% in the fine fraction compared to the bulk fraction. If

so, then evaluations of dioxin TEQs that are based only on analyses of bulk samples may tend to underestimate human health risk by 10-20%.

3.7 Quality Control Samples

Quality control samples that were analyzed as part of this study indicate that the data are reliable and accurate, as described below.

Method Blanks

Full TEQ(total) values for four method blanks ranged from 0.1 to 0.9 ppt (average = 0.5 ppt). This indicates that there is no significant source of PCDD, PCDF, or PCB contamination within the analytical laboratory.

Splits and Duplicates

Full and Quant TEQ values for duplicate and split samples are as follows:

Table 7. Evaluation of Precision in Replicate Analyses

Sample	Full TEQ(D/F) (ppt)		Quant TEQ(D/F) (ppt)	
	Value	Difference	Value	Difference
SP-4 SP-4 Dup	4.7 5.5	Delta = 0.8	3.8 4.3	Delta = 0.5
P-5 P-5 Split	11.9 11.4	Delta = 0.5	11.2 10.6	Delta = 0.4
SP-8 SP-8 Split	27.4 31.2	RPD = 13%	23.5 26.9	RPD = 13%

As seen, for samples with TEQ less than 25 ppt, the average absolute difference between samples pairs is about 0.4 to 0.8 ppt TEQ, well within the acceptability criterion of 1 MQL (about 5 ppt TEQ) that was established by the Project Plan (USEPA 1999). For samples with TEQ values above 25 ppt (about 5-times the MQL), the Relative Percent Difference (RPD) is 13%, also well within the acceptance criterion of 30% established by the Project Plan (USEPA 1999).

Performance Evaluation Samples

Analytical results for the certified soil standards (PE samples) obtained from the USEPA QATS laboratory are summarized below.

Table 8. Evaluation of Accuracy Using Certified PE Samples

PE Sample	Certified Conc. (ppt)	N	Measured TEQ(D/F) (ppt)	
			Full	Quant
Low Standard (bulk)	35	3	40.3 ± 12.6	40.2 ± 12.5
Medium Standard (bulk)	59	3	75.5 ± 1.9	74.5 ± 1.9

As seen, measured values for bulk PE samples are somewhat higher than but are still in reasonable accord with the expected (nominal) values.

Four samples of the "Clean Soil" PE sample provided by the QATS laboratory were also analyzed on an on-going basis throughout the study. This is the soil used by QATS contractors for spiking with TCDD-like congeners to produce the PE standard soils. This soil sample was estimated to contain less than 2 ppt TEQ in the bulk fraction, but this was not a certified value. The samples of Clean Soil analyzed in this study were sieved to isolate the fine fraction before analysis, so the expected value in the fine fraction is not known. However, analytical results were low (1.8 ± 0.5 ppt Full TEQ(D/F) and 1.9 ± 0.6 ppt Full TEQ(Total)), consistent with the estimated values in the bulk soil. Because these samples were submitted to CAS in parallel with field samples, these results establish that there is no significant source of contamination during the sample preparation or the sample analysis steps.

Laboratory Spikes

Sixteen different laboratory spikes were analyzed in association with the field samples from this study. Spike concentrations were 20 ppt for TCDD and TCDF, 100 ppt for each of the penta-, hexa- and hepta-PCDDs and PCDFs, and 200 ppt for OCDD, OCDF, and each of the PCBs. Based on this spiking mixture, the nominal TEQ(D/F) is 250 ppt, and the nominal TEQ(Total) is 272.5 ppt. Average recovery of individual PCDD/PCDF congeners ranged from 85% to 113%, with an average across all samples of 97%. Average recovery of individual PCBs ranged from 73% to 120%, with an average across all samples of 97%. When expressed as Full TEQ, recovery was 99% to 102% (mean = 100%) for TEQ(D/F), and was 100% to 103% (mean = 101%) for TEQ(Total). This indicates that matrix interference is not likely to be of concern.

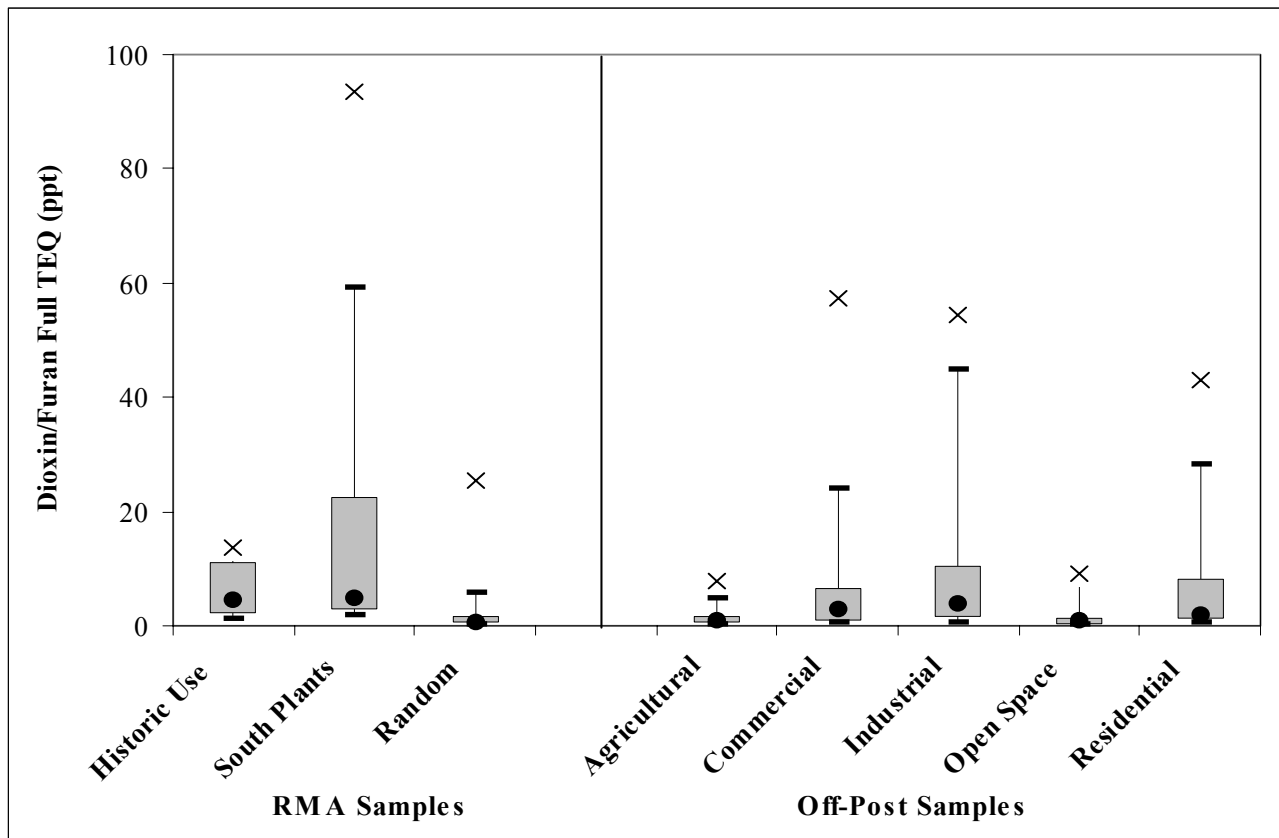
4.0 DISCUSSION

4.1 Comparison to Area-Wide Background Levels

Dioxins can be formed and released to the environment from a variety of sources, especially incinerators that burn medical and municipal wastes (USEPA 1994). In addition, dioxins can be formed in low levels from the combustion of coal and wood, and dioxins are released from power plants, wood burning furnaces, forest fires, etc. (USEPA 1998b). As a consequence of these multiple and widespread sources, dioxins are believed to be present in low concentrations in nearly all samples of surface soil.

Limited data are available in the literature on the concentrations of PCDDs and PCDFs in “background” soil. A summary of these data are presented in USEPA (2001c). In general, mean values for rural and urban areas are mainly in the 1-6 ppt range, although some lower and some higher values are reported. However, there are a number of limitations to these data (USEPA 2001c), so in order to strengthen the database for site-specific decision making, the USEPA Region 8 has recently completed studies of dioxin levels in a range of typical soils from multiple locations and land uses across the Denver Front Range (USEPA 2001c) and at random locations at RMA (USEPA 2001b). Appendix D contains maps that summarize the results of these studies, and Figure 5 compares the distribution of concentration values observed at historic use areas of RMA with values observed at sampling locations around the Denver Front Range area (USEPA 2001c) and with samples collected from random locations outside the core area at RMA (USEPA 2001b). As seen, the TEQ values at RMA historic use areas and at South Plants are somewhat higher than for other randomly selected areas at RMA and for open space or agricultural areas at off-post locations, but tend to overlap the range of values measured at commercial and industrial areas located in the Denver Front Range area. Multiple pair-wise comparisons using the Mann-Whitney rank sum test indicate that the data from the South Plants area at RMA are not statistically different from off-post industrial areas ($p = 0.258$), but are higher than each of the other off-post and on-post data sets ($p < 0.05$). Data from the purposeful sampling areas at RMA are not different from off-post industrial ($p = 0.923$), commercial ($p = 0.169$), or residential ($p = 0.247$) land uses, but are higher than random on-post samples and off-post agricultural and open space samples ($p < 0.01$).

It should also be noted that the historic use areas of RMA with the highest dioxin levels are scheduled for soil remediation due to the presence of organo-chlorine pesticide contamination. Once this remediation is complete, it is expected that dioxin levels throughout RMA will be approximately the same as for open space areas in the Denver Front Range area and will present no significant health risk to future Refuge workers, volunteers, or visitors.

Figure 5. Comparison of TEQ Levels to Denver Front Range Area Soils

4.2 Congener Composition

The congener composition of a soil sample may provide useful information about the source of the dioxin contamination, and helps to reveal which specific congeners are contributing the majority of the risk.

Appendix A shows the relative (percent) contribution of each of the 29 congeners to the total TEQ in each of the soil samples in this study. The mean contribution of each congener (percent contribution within a sample averaged across all samples) to TEQ is summarized in Table 9. As seen, most of the Full TEQ(Total) is contributed by PCB-126 along with a number of penta- and hexa-PCDDs and PCDFs, including 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, and 2,3,4,6,7,8-HxCDF.

Appendix B1 presents a series of graphs showing the absolute chemical concentrations and TEQ contributions of each of the 29 congeners in each of the field soil samples collected during this study. Appendix B2 shows the aggregate concentrations and TEQ contributions for each of the five homologue classes of the 17 TCDD-like dioxins and furans. Appendix B3 shows the relationships between aggregate concentrations and TEQ contributions of dioxins compared to furans. Appendix B4 presents similar concentration graphs for QA samples. In all cases, greater emphasis is placed on the quantitative concentration data than the full concentration data for evaluation of congener concentration profiles.

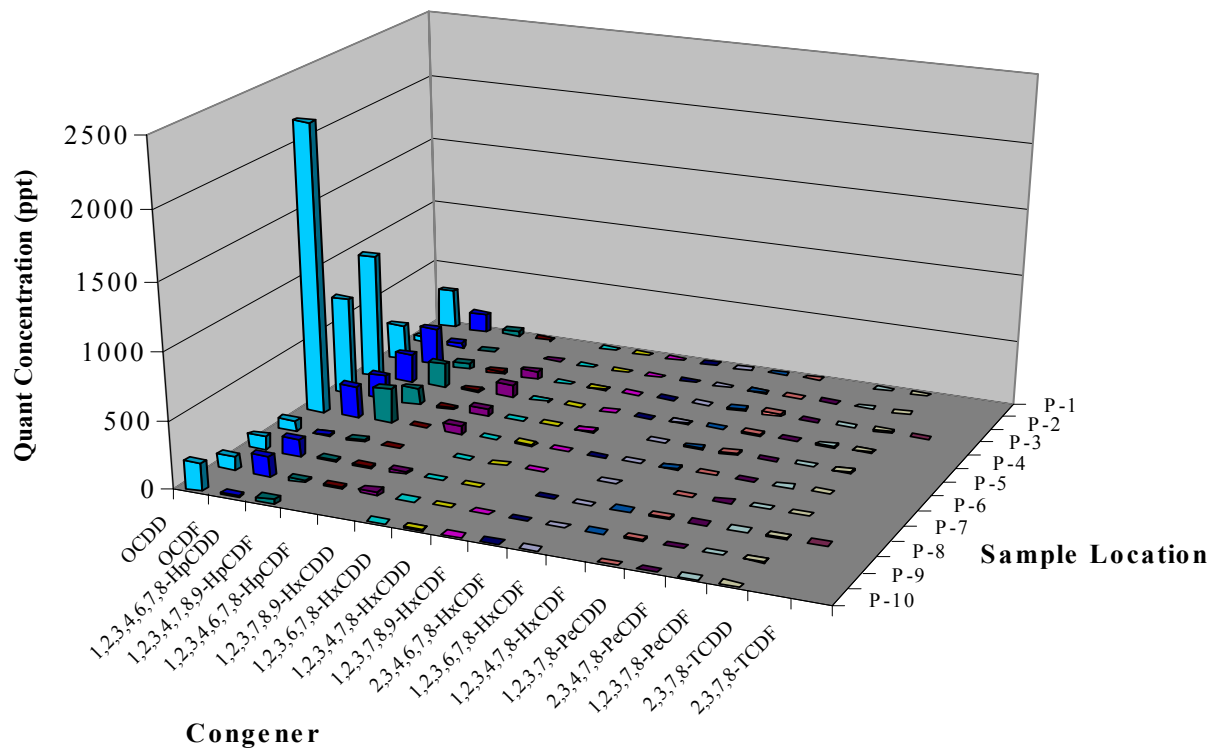
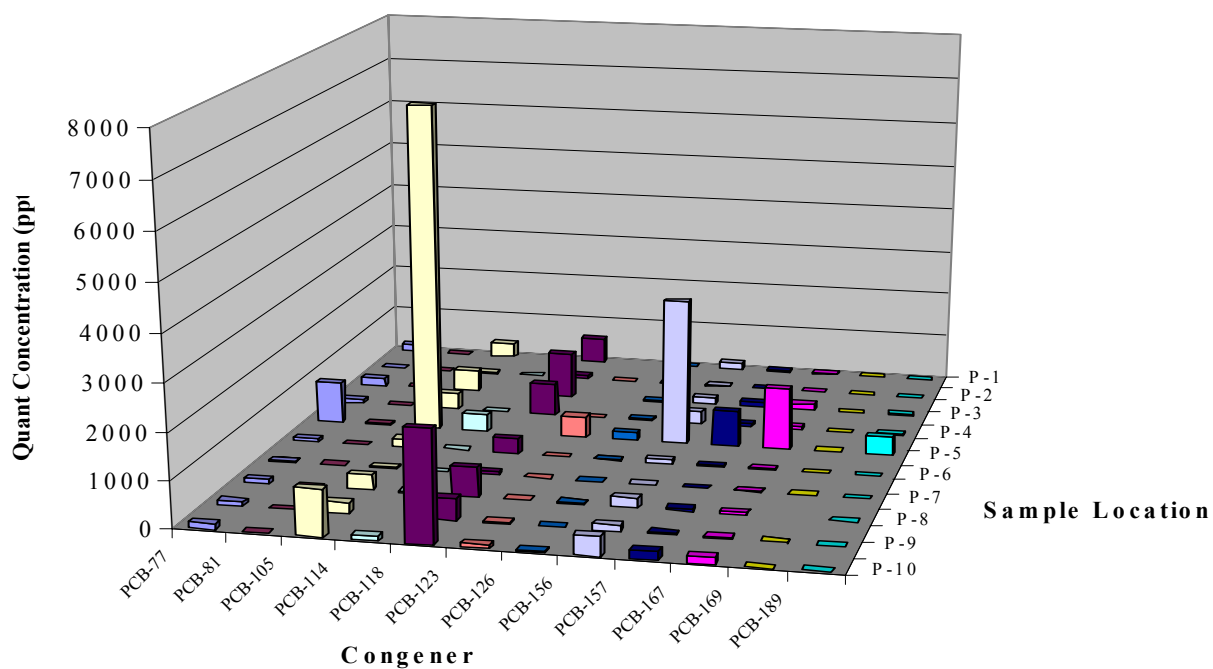
Figure 6 summarizes the average quantitative congener concentration pattern in RMA soil samples from the historic use areas. The upper panel shows congeners in the PCDD/PCDF class, while the lower panel shows congeners in the PCB class. As seen in the upper panel, the primary congeners in the PCDD/PCDF group are OCDD and OCDF, along with lower levels of several hepta- and hexa-PCDDs and PCDFs. As seen in the lower panel, several PCBs are usually present, primarily PCB-105 and PCB-118, with lower levels of PCB-77, PCB-156, and PCB-167.

A more detailed and quantitative analysis of the congener concentration values in surface soil samples from the historic use areas of RMA along with results from other locations at RMA and from multiple locations and land uses around the Denver Front Range area will be presented in a subsequent report.

Table 9. Average Contribution of Congeners to TEQ

Analyte	Mean Contribution to TEQ (Total)			
	South Plants		Purposeful	
	Full	Quant	Full	Quant
2,3,7,8-TCDF	1.1%	0.0%	1.5%	0.0%
2,3,7,8-TCDD	3.3%	1.3%	2.5%	0.9%
1,2,3,7,8-PeCDF	5.7%	7.0%	2.1%	2.3%
2,3,4,7,8-PeCDF	12.0%	13.8%	11.0%	10.7%
1,2,3,7,8-PeCDD	7.4%	2.2%	13.0%	12.2%
1,2,3,4,7,8-HxCDF	20.6%	25.3%	7.7%	9.3%
1,2,3,6,7,8-HxCDF	11.3%	13.6%	4.7%	5.4%
2,3,4,6,7,8-HxCDF	5.4%	3.6%	3.5%	2.9%
1,2,3,7,8,9-HxCDF	5.0%	2.8%	2.1%	0.8%
1,2,3,4,7,8-HxCDD	1.1%	1.0%	1.6%	1.4%
1,2,3,6,7,8-HxCDD	1.7%	1.8%	3.3%	3.9%
1,2,3,7,8,9-HxCDD	1.4%	0.7%	2.8%	3.2%
1,2,3,4,6,7,8-HpCDF	1.3%	0.0%	3.0%	3.2%
1,2,3,4,7,8,9-HpCDF	2.3%	2.8%	0.8%	0.8%
1,2,3,4,6,7,8-HpCDD	3.5%	4.5%	7.1%	8.3%
OCDF	0.4%	0.4%	0.2%	0.2%
OCDD	0.3%	0.3%	0.5%	0.6%
PCB-77	0.1%	0.1%	0.2%	0.2%
PCB-81	0.0%	0.0%	0.0%	0.0%
PCB-105	0.6%	0.5%	1.1%	0.7%
PCB-114	0.2%	0.1%	0.2%	0.2%
PCB-118	1.2%	0.8%	1.7%	1.0%
PCB-123	0.0%	0.0%	0.1%	0.0%
PCB-126	13.1%	16.5%	26.6%	29.6%
PCB-156	1.0%	0.7%	2.0%	1.7%
PCB-157	0.2%	0.2%	0.5%	0.5%
PCB-167	0.0%	0.0%	0.0%	0.0%
PCB-169	0.2%	0.1%	0.2%	0.2%
PCB-189	0.0%	0.0%	0.0%	0.0%
PCDDs/PCDFs	83.4%	81.2%	67.4%	65.8%
PCBs	16.6%	18.9%	32.6%	34.2%
Total	100.0%	100.0%	100.0%	100.0%

Cells greater than 5% have been shaded to highlight the main contributors

Figure 6. Average Congener Concentration Profile in Historic Use RMA Soils**PCDD/PCDFs****PCBs**

4.3 Dependence of TEQ on Soil Characteristics

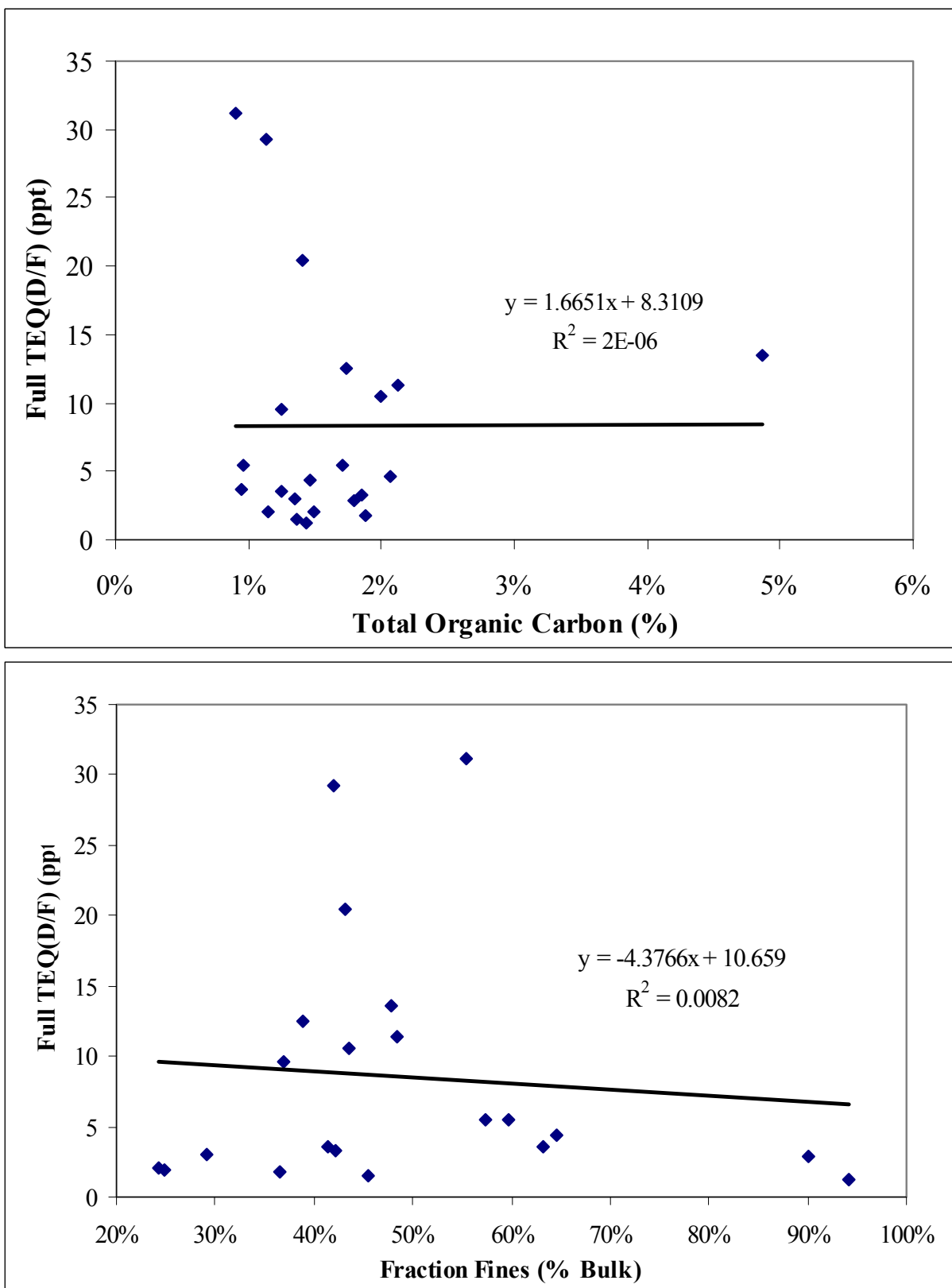
Binding of dioxins to soil particles is a physical process that might be expected to depend on the total organic carbon (TOC) content of the soil, as well as the surface-area-to-mass ratio (i.e., the particle size distribution). Such a dependence of TEQ levels on soil characteristics has been noted by Rogowski et al. (1999), although these data are somewhat limited by use of TEQ values calculated from congener concentrations that were largely below the MDL.

Figure 7 (Panel A) summarizes the relationship between Full TEQ(D/F) and soil TOC. As seen, TOC levels ranged from less than 1% up to about 5% in the soil samples, while Full TEQ(D/F) levels ranged from about 0.1 to more than 30 ppt. The slope of the best-fit linear regression line through the data is not statistically different from zero ($p > 0.5$), and the coefficient of determination is essentially zero ($R^2 = 2E-06$). This indicates that the TOC value is not a significant determinant of the TEQ value, at least in these soil samples.

Figure 7 (Panel B) shows the relation between Full TEQ(D/F) and the mass fraction of the raw field sample that passes a fine screen. As above, the slope of the best-fit linear regression line is not statistically different from zero ($p > 0.5$), and the coefficient of determination is very low ($R^2 = 0.008$). This indicates that the fraction of fine particles in a soil is not a significant determinant of TEQ levels, at least in these soil samples.

5.0 SUMMARY AND CONCLUSIONS

Using perimeter areas of RMA as a frame of reference, the concentration of dioxins (including both PCDD/PCDF and PCB congeners) is slightly elevated in samples of soil collected from areas historically used for chemical manufacturing operations (South Plants) or waste disposal. The spatial pattern of contamination does not suggest that any significant off-site releases have occurred, and even the highest on-site levels are far below a level of health concern to on-site workers. Concentration levels tend to overlap those found at other industrial and commercial areas around the Denver Front Range area. Once remediation is complete, it is expected that dioxin levels throughout RMA will be approximately the same as for open space areas in the Denver Front Range area and will present no significant health risk to future Refuge workers, volunteers, or visitors.

Figure 7. Dependence of TEQ on Soil Characteristics

6.0 REFERENCES

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